

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 July 2003 (03.07.2003)

PCT

(10) International Publication Number  
**WO 03/054958 A1**

(51) International Patent Classification<sup>7</sup>: **H01L 23/433**,  
23/373, C01B 31/02

(21) International Application Number: PCT/US02/40515

(22) International Filing Date:  
17 December 2002 (17.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/027,442 20 December 2001 (20.12.2001) US

(71) Applicant: **INTEL CORPORATION** [US/US]; (a  
Delaware Corporation), 2200 Mission College Boulevard,  
Santa Clara, CA 95052 (US).

(72) Inventors: **MONTGOMERY, Stephen**; 1821 6th Avenue  
Westt, #7, Seattle, WA 98119 (US). **HOLAKERE, Ven**;  
4550 Central Parkway, Dublin, CA 94568 (US).

(74) Agent: **STEFFEY, Charles, E.**; Schwegman, Lundberg,  
Woessner & Kluth, P.A., P.O. Box 2938, Minneapolis, MN  
55402 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,  
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC,  
VN, YU, ZA, ZM, ZW.

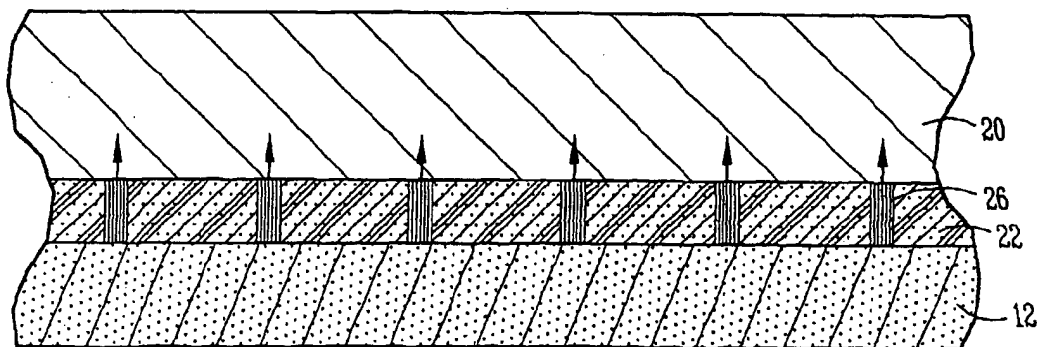
(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK,  
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: CARBON NANOTUBE THERMAL INTERFACE STRUCTURES



(57) Abstract: The invention relates to a process of forming a thermal interface that employs carbon nanotubes to reduce thermal resistance between an electronic device and a cooling solution. Bundles of aligned nanotubes receive injected polymeric material to produce a polymeric/carbon composite which is then placed between the electronic device and a heat sink or other cooling solution.

WO 03/054958 A1

## CARBON NANOTUBE THERMAL INTERFACE STRUCTURES

## FIELD OF THE INVENTION

The present invention relates generally to providing cooling solutions to electronic  
5 circuits, and, more specifically to the fabrication of a thermal interface structure using  
carbon nanotubes to improve thermal performance to a die containing an electronic circuit.

## BRIEF DESCRIPTION OF THE DRAWINGS

In order that the manner in which the embodiments of the invention are obtained, a  
more particular description of the invention briefly described above will be rendered by  
10 reference to specific embodiments thereof which are illustrated in the appended drawings.  
Understanding that these drawings depict only typical embodiments of the invention that  
are not necessarily drawn to scale and are not therefore to be considered to be limiting of  
its scope, the invention will be described and explained with additional specificity and  
detail through the use of the accompanying drawings in which:

15 **Figure 1** is an elevation view of a flip chip electronic device which is coupled to a  
cooling plate using a thermal interface according to an embodiment of the present  
invention;

**Figure 2** is a perspective view of a portion of the thermal interface of Figure 1,  
with polymer additive, showing carbon nanotube array bundles;

20 **Figure 3** is a perspective illustrational schematic view of a thermal interface  
showing, carbon nanotube bundles, in exaggerated scale distributed over the surface of the  
thermal interface;

**Figure 4** is an elevational cross-section of the thermal interface structure depicted  
in Figure 3 showing the flow of heat from the surface of the electronic device to the heat  
25 sink; and

Figure 5 is a flow chart of a process for producing a thermal interface structure according to one embodiment of the present invention.

Figure 6 is a flow chart of a process for providing a thermal path between two objects according to an embodiment of the present invention.

5

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a thermal interface structure and method of forming it from a matrix of oriented carbon nanotubes projecting from a substrate.

It will be readily understood to those skilled in the art that various other changes in  
10 the details, material, and arrangements of the parts and method stages which have been described and illustrated in order to explain the nature of this invention may be made without departing from the principles and scope of the invention as expressed in the claims.

In Figure 1, a portion of an electronic device such as a computer 10 is illustrated in  
15 an elevation view. In device 10, a silicon die 12 which, in the embodiment shown, is mounted in a flip-chip ball grid array on an organic substrate 14 which is, in turn, mounted on a further substrate 16 and secured by solder balls 18. A cooling solution such as heat sink plate 20 is coupled to the surface of die 12 by a thermal interface structure 22 in the embodiment shown.

20 A variety of thermal interface materials have been used in the past to reduce thermal resistance between a die and a cooling solution. In some applications, thermal grease is used for the thermal interface material since such materials have high bulk thermal conductivity and readily conform to surface irregularities in the heat sink and the device. Use of thermal greases, however, have the disadvantage of possible pump out and  
25 phase separation of the grease as the die is heated and undergoes thermal warping due to

differences in the coefficient of thermal expansion between die 12 and organic substrate

14. In other applications, adhesives such as epoxy are used as thermal interface material

but have the disadvantage of requiring a cure process after their application. Various

thermal gels such as silicones or certain olefins may also be used as thermal interface

5 materials but they also require curing after application and have lower thermal

conductivity than thermal grease. Certain elastomers such as urethane rubber have high

bulk conductivity but suffer from high contact resistance and require that high pressure of

at least 100 psi be applied at the thermal junction to provide adequate thermal coupling.

Finally, certain phase change materials such as low molecular weight polyesters have been

10 used but also suffer from the fact that their thermal conductivity is less than that of thermal

grease. The thermal conductivity of thermal interface materials commonly used have a

conductivity value of about 10 W/m-°K.

In one embodiment of the invention, a thermal interface structure is formed from  
an array of aligned carbon nanotubes in a polymeric interstitial material. Since the thermal

15 conductivity of the carbon nanotubes is on the order of 3000 W/m-°K using them in a  
thermal interface structure will substantially increase its thermal conductivity.

In Figure 2, a portion of a substrate 28 having an array of spaced bundles 24 of  
carbon nanotubes 26 projecting from the surface thereof is illustrated in highly enlarged  
form prior to injection of a polymer additive. Such arrays are available from Nano-Lab,

20 Inc. which manufactures them under a chemical vapor deposition process described in an  
article of Dr. Z. F. Ren in Science, 282, 1105 (1998). The array of bundles 24 of  
nanotubes 26 which are produced in accordance with the process are grown on a variety of  
substrates 28 including glass and silicon. The nanotubes 26 grown on substrate 28 are  
aligned so that the majority of the nanotubes are oriented generally parallel to each other

differences in the coefficient of thermal expansion between die 12 and organic substrate

14. In other applications, adhesives such as epoxy are used as thermal interface material

but have the disadvantage of requiring a cure process after their application. Various

thermal gels such as silicones or certain olefins may also be used as thermal interface

5 materials but they also require curing after application and have lower thermal

conductivity than thermal grease. Certain elastomers such as urethane rubber have high

bulk conductivity but suffer from high contact resistance and require that high pressure of

at least 100 psi be applied at the thermal junction to provide adequate thermal coupling.

Finally, certain phase change materials such as low molecular weight polyesters have been

10 used but also suffer from the fact that their thermal conductivity is less than that of thermal

grease. The thermal conductivity of thermal interface materials commonly used have a

conductivity value of about 10 W/m-°K.

In one embodiment of the invention, a thermal interface structure is formed from  
an array of aligned carbon nanotubes in a polymeric interstitial material. Since the thermal

15 conductivity of the carbon nanotubes is on the order of 3000 W/m-°K using them in a  
thermal interface structure will substantially increase its thermal conductivity.

In Figure 2, a portion of a substrate 28 having an array of spaced bundles 24 of  
carbon nanotubes 26 projecting from the surface thereof is illustrated in highly enlarged  
form prior to injection of a polymer additive. Such arrays are available from Nano-Lab,

20 Inc. which manufactures them under a chemical vapor deposition process described in an  
article of Dr. Z. F. Ren in Science, 282, 1105 (1998). The array of bundles 24 of  
nanotubes 26 which are produced in accordance with the process are grown on a variety of  
substrates 28 including glass and silicon. The nanotubes 26 grown on substrate 28 are  
aligned so that the majority of the nanotubes are oriented generally parallel to each other

and perpendicular to the substrate 28 from which they project. The heights of the nanotubes are typically quite similar.

A thermal interface structure 22 according to the present invention may be formed from a substrate 28 upon which nanotube bundles 26 are supported. A polymeric  
5 interstitial material 30 is injected around the nanotube bundles 26 to support the nanotubes. Suitable polymeric materials include polycarbonate, polypropylene and acetal. After addition of polymeric material 30, the substrate 28 upon which the nanotubes were originally formed is removed. Suitable processes for removal of substrate 28 are mechanical grinding or chemical etching.

10 As shown in Figure 2, the length L and width W of thermal interface structure 22 are selected to provide a substantial heat exchange surface while falling within the outlines of the exposed surface of die 12. In one embodiment the length and width are 2 cm and 1 cm.

The maximum thickness t of the thermal interface structure is limited by the length  
15 of the carbon nanotubes but will typically fall within the range of about 5 to 20 microns. Of course, increasing the thickness of the thermal interface structure 22 will increase the thermal impedance of the path between the die and the heat sink. As shown in Figure 4, the carbon nanotubes are oriented generally parallel to each other and perpendicular to the top and bottom surfaces of structure 22, since they provide their greatest thermal  
20 conductivity along their longitudinal axes and it is desirable to have the conducted heat follow the shortest path between die 12 and heat sink 20.

Figure 5 is a flow chart outlining an embodiment of the method of forming the thermal intermediate structure. In operation 52 an array 24 of nanotube bundles 26 includes a substrate 28 from which nanotubes 26 project. The array is embedded with an  
25 interstitial material 30 which is a polymeric material selected from the group consisting of

polycarbonate, polypropylene, polyacetal, polyoxymethylene and polyformaldehyde. The interstitial material 30 is thermoplastic and is injected in molten form to embed it in the array to form an intermediate structure.

In operation 54 any excess interstitial material 30 is removed from the intermediate  
5 and the substrate 28 upon which the nanotube bundles were originally grown. The removal can be performed by a chemical mechanical polishing process or by mechanical grinding. At the conclusion of operation 54, the thermal intermediate structure is completed. The carbon nanotubes remained aligned with each other throughout the forming of the structure and, after removal of excess interstitial material and the original  
10 substrate, the ends of the carbon nanotubes are at the surfaces of the thermal intermediate structure which engage the object to be cooled and the cooling solution surface to which the thermal intermediate structure couples it.

If the thermal intermediate structure provides thermal coupling between surfaces of two objects and the thermal intermediate structure is under pressure, yielding of the  
15 interstitial material will assure that the carbon nanotubes make secure thermal contacts with the surfaces of the objects which sandwich it, despite the presence of irregularities in the flatness of the surfaces.

Figure 6 shows a process for providing a thermal coupling between two objects. In operation 62, a nanotube array is coupled to one of the objects. In one embodiment, the  
20 nanotube array may actually be grown on the surface of the object rather than on a separate substrate. In that embodiment it is necessary that the temperatures and other conditions under which the carbon nanotubes are formed be within the temperature ranges and exposure times permitted by the object upon which the nanotube array is grown. In this embodiment the injection with the interstitial material in operation 64 and the removal

of the excess material are carried out in much the same manner of the operations shown in Figure 5.

In another embodiment, operation 62 is performed after the nanotubes are formed on a separate substrate and after the interstitial material has been applied in operation 64  
5 and the excess material removed in operation 66.

In the embodiments the process shown in Figure 6 discussed above, the operation 68 involves coupling the other surface of the array to the other of the two objects. In one embodiment one of the objects may be a cooling solution such as a heat sink and the other a semiconductor die. In one embodiment, either of the objects can receive carbon  
10 nanotubes as they are grown in operation 62. Using that process, an additional advantage of a particularly strong thermal bond to that object is obtainable.

The foregoing description of the specific embodiments reveals the general nature of the invention sufficiently that others can, by applying current knowledge, readily modify and/or adapt it for various applications without departing from the generic concept  
15 and therefore such adaptations and modifications are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments.

It is to be understood that the phraseology and terminology employed herein is for the purpose of description and not of limitation. Accordingly, the invention is intended to embrace all such alternatives, modifications, equivalents and variations as fall within the  
20 spirit and broad scope of the appended claims.



## CLAIMS

What is claimed is.

1. A thermal interface structure comprising:  
at least one carbon nanotube oriented substantially parallel to a desired heat  
5 transfer axis of the thermal interface; and  
an interstitial material in which the nanotubes are embedded.
2. The structure of claim 1, wherein the structure has a first surface to contact  
a surface of a circuit die and a second surface to contact a surface of a cooling solution, the  
first and second surfaces being substantially parallel to each other.
- 10 3. The structure of claim 2, wherein the thickness of the structure from the  
first surface to the second surface is about 5 to 20 microns.
4. The structure of claim 1 wherein the interstitial material is a polymeric  
material.
5. The structure of claim 4, wherein the polymeric material is selected from  
15 the group consisting of polycarbonate, polypropylene, polyacetal, polyoxymethylene and  
polyformaldehyde.
6. A thermal interface comprising:  
at least one bundle of carbon nanotubes, the bundles oriented substantially  
parallel to each other and to a heat transfer flow path of the thermal interface; and  
20 an interstitial material between the bundles of nanotubes.

7. The thermal interface of claim 6 wherein the interstitial material is a polymeric material.
8. The thermal interface of claim 6 wherein the thermal interface has first and second generally planar surfaces which are each substantially perpendicular to the heat transfer path.
9. A heat transfer structure for use with a semiconductor die comprising:  
a heat sink having a surface to couple to the die; and  
a thermally conductive element comprising a first surface coupled to the heat sink and a second surface coupled to the semiconductor die, the thermally conductive element comprising a plurality of carbon nanotubes oriented with their axes substantially perpendicular to the first and second surfaces.
10. The heat transfer structure of claim 9 wherein the thermally conductive element also comprises an interstitial bonding material interspersed among the carbon nanotubes.
11. The heat dissipating structure of claim 10 wherein the interstitial bonding material is a polymeric material selected from the group consisting of polycarbonate, polypropylene, polyacetal, polyoxymethylene and polyformaldehyde.
12. The heat dissipating structure of claim 9 wherein the thermally conductive element has a surface area that is substantially the same as the surface area of the die.
13. The heat dissipating structure of claim 12 wherein the thickness of the thermally conductive element is between 10 and 50 microns.

14. An electronic assembly comprising at least one integrated circuit package comprising:
- at least one integrated circuit die;
  - a heat sink having a surface coupled to the die; and
  - 5 a thermally conductive element comprising a first surface coupled to the heat sink and a second surface coupled to the die, the thermally conductive element comprising a plurality of carbon nanotubes oriented with their axes substantially perpendicular to the first and second surfaces.
15. The electronic assembly of claim 14 wherein the thermally conductive element also comprises an interstitial material embedded among the carbon nanotubes.
16. The electronic assembly of claim 15 wherein the interstitial material is a polymeric material selected from the group consisting of polycarbonate, polypropylene, polyacetal, polyoxymethylene and polyformaldehyde.
17. A data processing system comprising:
- a bus coupling components to the data processing system;
  - a display coupled to the bus;
  - external memory coupled to the bus; and
  - a processor coupled to the bus and comprising an electronic assembly
- including at least one electronic package comprising:
- at least one integrated circuit die;
  - a heat sink having a surface coupled to the die; and
  - a thermally conductive element comprising a first surface coupled to the heat sink and a second surface to couple to the die, the thermally conductive element comprising a plurality of carbon nanotubes oriented with their axes
- substantially perpendicular to the first and second surfaces.
18. The data processing system of claim 17 wherein the thermally conductive element comprises an interstitial material interspersed among the carbon nanotubes.

19. The data processing system of claim 18 wherein the interstitial material is a polymeric material selected from the group consisting of polycarbonate, polypropylene, polyacetal, polyoxymethylene and polyformaldehyde.

20. A method of fabricating a thermal interface structure comprising:  
5 embedding an array of substantially aligned carbon nanotubes in an interstitial material to form an intermediate having a layer of substantially aligned carbon nanotubes embedded therein; and  
removing excess material from the intermediate to provide a thermal  
10 interface structure having a first substantially planar surface for engaging a surface of one object and a second substantially planar surface for engaging a surface of another object, the first and second surfaces oriented substantially perpendicular to the substantially aligned carbon nanotubes.

21. The method of claim 20 wherein the array of substantially aligned carbon nanotubes also comprises a substrate from which the carbon nanotubes project and  
15 wherein the removing of excess material also comprises removing at least a portion of the substrate.

22. The method of claim 20 wherein removing excess material comprises chemical mechanical polishing of the intermediate.

23. The method of claim 20 wherein removing excess material comprises  
20 etching the intermediate.

24. A method of providing a thermal intermediate between two objects comprising:  
providing an array of substantially aligned carbon nanotubes coupled to one  
of the objects;  
25 embedding the array of substantially aligned carbon nanotubes in an interstitial material to form a layer of substantially aligned carbon nanotubes embedded therein; and  
coupling the array to the other object.

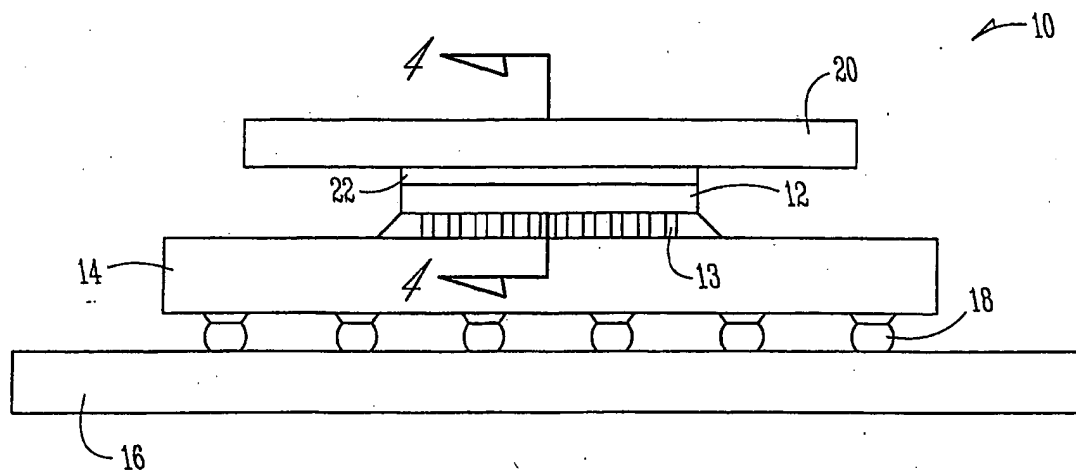
25. The method of claim 24 wherein providing the array coupled to the object comprises forming the carbon nanotubes on the surface of the object

26. The method of claim 24 wherein providing the array coupled to the object comprises

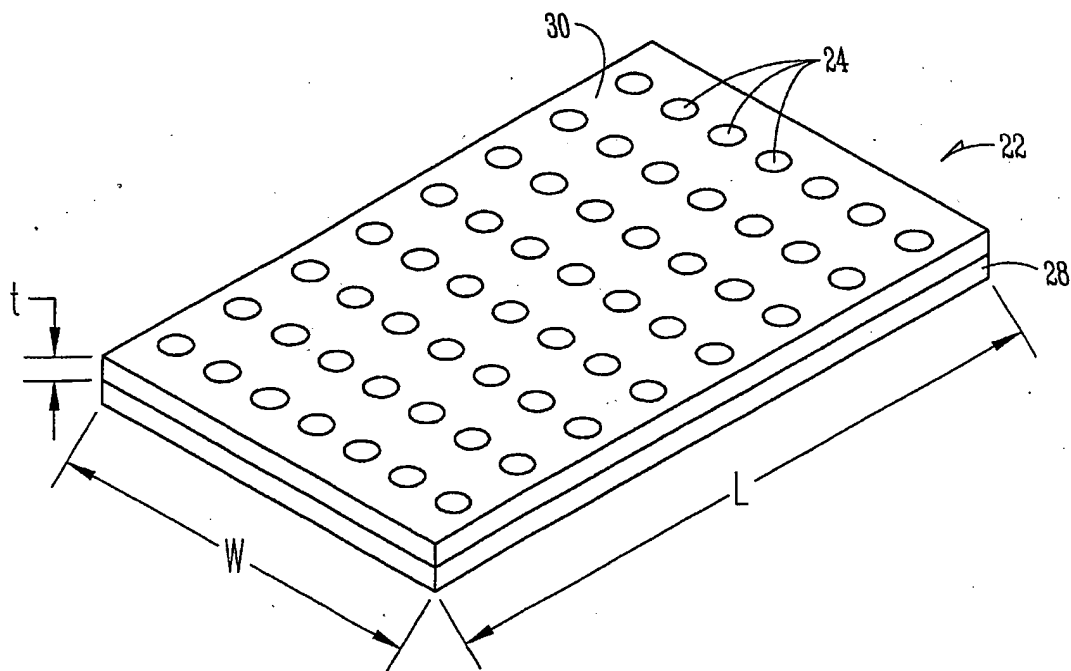
- 5       forming the array on a substrate;  
      embedding the array in an interstitial material;  
      removing the substrate; and  
      coupling the array to the object.

## Glossary

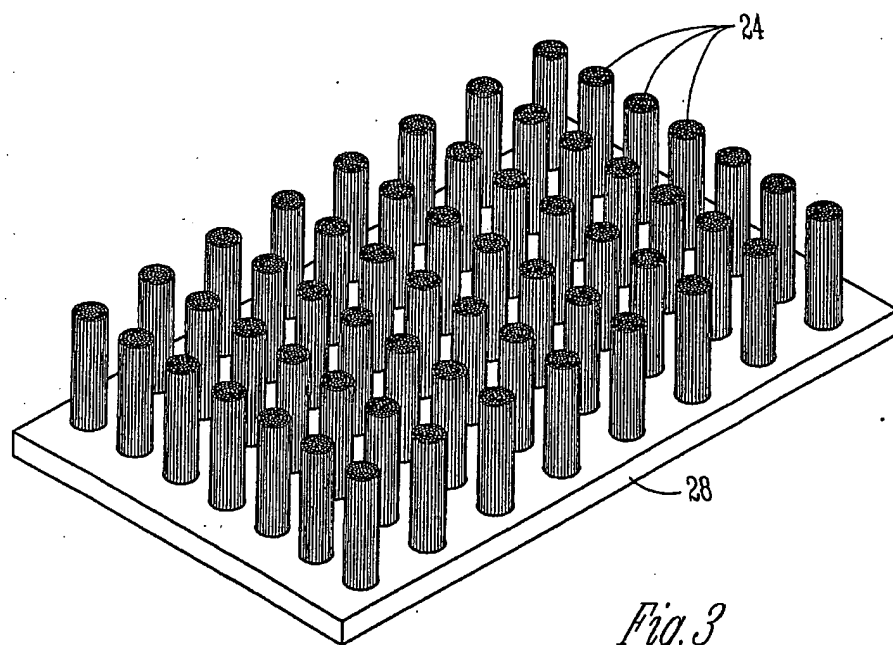
	10	device
	12	silicon die
5	13	
	14	organic substrate
	15	
	16	further substrate
	17	
10	18	solder balls
	19	
	20	heat sink plate
	21	
	22	thermal interface structure
15	23	
	24	array 24
	25	
	26	of bundles of nanotubes
	27	
20	28	substrate (for nanotube bundles)
	29	
	30	polymeric interstitial material
	31	
	32	
25		



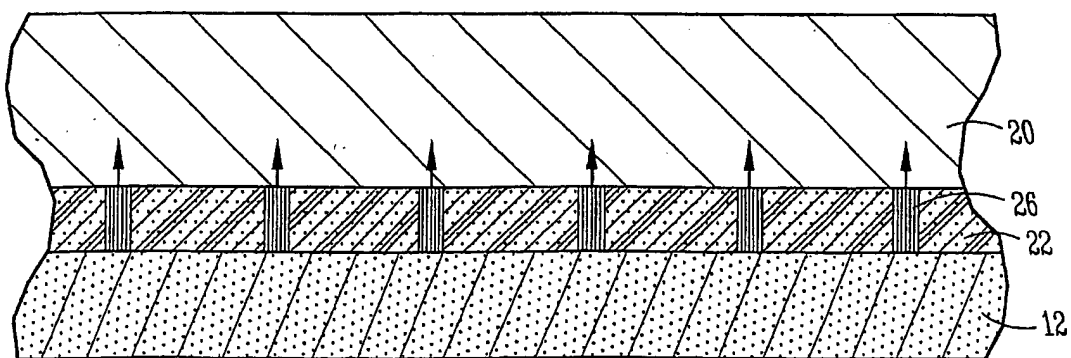
*Fig. 1*



*Fig. 2*

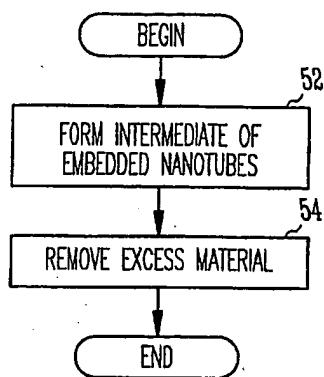
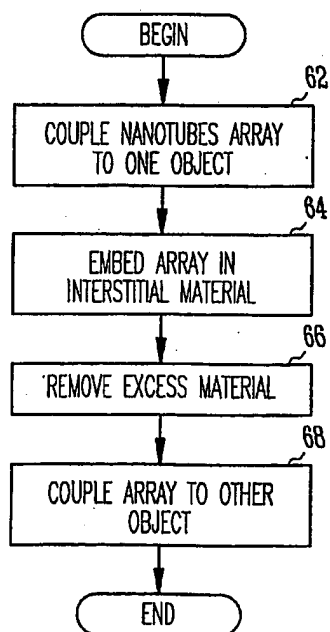


*Fig. 3*



*Fig. 4*



*Fig. 5**Fig. 6*

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/40515

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L23/433 H01L23/373 C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 965 267 A (LYNCH DAVID G ET AL) 12 October 1999 (1999-10-12)	1,2,4, 6-10,12, 14,15, 24,25
A	the whole document	20
P,X	US 6 407 922 B1 (ECKBLAD MICHAEL Z ET AL) 18 June 2002 (2002-06-18)	1,2,4, 6-10,12, 14,15, 17,18, 24,25
	the whole document	
X	WO 01 92381 A (BARRERA ENRIQUE V ;UNIV RICE WILLIAM M (US); LOZANO KAREN (US); CH) 6 December 2001 (2001-12-06)	1,4-11, 20,24,25
A	the whole document	14,17
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

26 March 2003

Date of mailing of the international search report

02/04/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Zeisler, P

## INTERNATIONAL SEARCH REPORT

International A tion No

PCT/US 02/40515

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 054 036 A (FINA RESEARCH) 22 November 2000 (2000-11-22)	1,2,4, 6-10,24, 25
A	the whole document	14,17
A	ANDREWS R ET AL: "NANOTUBE COMPOSITE CARBON FIBERS", APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, VOL. 75, NR. 9, PAGE(S) 1329-1331 XP000868231 ISSN: 0003-6951 the whole document	4,16
X	WO 01 30694 A (SMALLEY RICHARD E ;UNIV RICE WILLIAM M (US); SMITH KEN A (US); CHI) 3 May 2001 (2001-05-03)	1,2,4, 6-10
A	the whole document	14,16
A	EP 1 109 218 A (POLYMATECH CO LTD) 20 June 2001 (2001-06-20) the whole document	1,6
A	WO 00 33628 A (INTEL CORP ;BROWNELL MICHAEL P (US)) 8 June 2000 (2000-06-08) the whole document	1,6

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/40515

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5965267	A	12-10-1999	US 5780101 A	14-07-1998
US 6407922	B1	18-06-2002	NONE	
WO 0192381	A	06-12-2001	AU 2577101 A	11-12-2001
			EP 1244730 A1	02-10-2002
			WO 0192381 A1	06-12-2001
EP 1054036	A	22-11-2000	EP 1054036 A1	22-11-2000
			AU 4565900 A	05-12-2000
			WO 0069958 A1	23-11-2000
			EP 1181331 A1	27-02-2002
			JP 2002544356 T	24-12-2002
			US 6331265 B1	18-12-2001
WO 0130694	A	03-05-2001	AU 2248301 A	08-05-2001
			CN 1359352 T	17-07-2002
			EP 1226093 A2	31-07-2002
			WO 0130694 A1	03-05-2001
EP 1109218	A	20-06-2001	JP 2001172398 A	26-06-2001
			EP 1109218 A2	20-06-2001
			US 2001004546 A1	21-06-2001
WO 0033628	A	08-06-2000	AU 1616300 A	19-06-2000
			WO 0033628 A1	08-06-2000